A miniaturized Schottky diode hydrogen and hydrocarbon sensor and the method of making same is disclosed and claimed. The sensor comprises a catalytic metal layer, such as palladium, a silicon carbide substrate layer and a thin barrier layer in between the catalytic and substrate layers made of palladium oxide (PdO₂). This highly stable device provides sensitive gas detection at temperatures ranging from at least 450 to 600°C. The barrier layer prevents reactions between the catalytic metal layer and the substrate layer. Conventional semiconductor fabrication techniques are used to fabricate the small-sized sensors. The use of a thicker palladium oxide barrier layer for other semiconductor structures such as a capacitor and transistor structures is also disclosed.

4 Claims, 9 Drawing Sheets
Science
Si-based hydrogen
http://www.nasa.gov/WWW/chemsensors/.
Oct. 2002
* cited by examiner
Current and Voltage Sweep of Pt/PdOx/SiC at 450° at 467 Hours

Fig. 2
Current and Voltage Sweep of Pd/PdOx/SiC at 450°C at 715 Hours

FIG. 2A

Current (A)

Voltage (V)

1x10^-1 1x10^-2 1x10^-3 1x10^-4 1x10^-5 1x10^-6 1x10^-7 1x10^-8 1x10^-9 1x10^-10 1x10^-11 1x10^-12
Diode

FIG. 5

501 Metal(s) or Metal Alloys
502 PdOx layer (50Å to 200Å)
503 n-type epi
504 SiC wafer
505 Backside Contact
FIG. 6

Transistor

600 GATE

601 Metal(s) or Metal Alloys

602 PdOx layer

603 n-type epi

604 SiC p-type

605 Backside Contact

606 Source

607 Drain

608 Source
Schottky Diode Pd/PdOx/SiC Tested at 450°C, 0.4V

Current in Air
Current in Hydrogen
Gain

Current Output (mA) and Gain (Current in Hydrogen/Current in Air)

Time (Hrs)

FIG. 7
Schottky Diode Pt/PdOx/SiC Tested at 450C and 600C, 1V

0 to 169 H, 450C
170 H to 216 H, 600C
217 H to 609 H, 450C,
610 H to 680 H, 600C
681 H to 776 H, 450C

FIG. 8
US 7,389,675 B1

MINIATURIZED METAL (METAL ALLOY)/
POD₃/SIC HYDROGEN AND
HYDROCARBON GAS SENSORS

ORIGIN OF THE INVENTION

The invention described herein was made by employees and by an employee of a contractor of the United States Government, and may be manufactured and used by the government for governmental purposes without the payment of any royalties therein and therefor.

FIELD OF THE INVENTION

The invention is in the field of hydrogen and hydrocarbon sensing. In particular hydrogen and hydrocarbon gas are detected using a microfabricated, miniaturized Schottky diode containing a stable interlayer of POD₃ between a top catalytic sensing layer and SiC substrate.

BACKGROUND OF THE INVENTION

U.S. Pat. No. 5,670,115 to Cheng et al. discloses a thin film of palladium to catalyze the dissociation of Hydrogen Gas. Detection and measurement of the hydrogen gas is accomplished with an amorphous metal film consisting of nickel and zirconium that has a resistance which varies with the concentration of dissolved hydrogen. This device consists of only two layers and operates in the range of room temperature to 150° C. According to Cheng, palladium film serves to dissociate hydrogen molecules at the Pd surface and the hydrogen atoms diffuse into the palladium film. Hydrogen atoms diffuse through the thin palladium film into the underlying nickel-zirconium film and dissolve therein. Hydrogen atoms flow into and out of the films depending on the hydrogen gas concentration. The electrical resistivity of the nickel-zirconium film increases as the content of the dissolved hydrogen increases. The palladium layer also serves as a barrier to oxidation of the underlying nickel-zirconium film. See, the '115 patent to Cheng at col. 2, ins. 1 et seq.

U.S. Pat. No. 3,709,810 to Grubb et al. discloses the use of an improved hydrogen ion selective sensing electrode comprising a palladium oxide coated surface on a palladium coated base member along with a reference electrode in contact with an electrolyte chamber.

U.S. Pat. No. 6,184,564 to Gould discloses a Schottky diode having a palladium silicide on silicon barrier in which the barrier height is adjusted by adding a small quantity of another metal during the deposition of the palladium. The palladium silicide includes palladium and a small quantity of another metal. The additional metal is chosen depending on whether barrier height is raised or lowered. See col. 1, ins. 59 et seq. of the '564 patent to Gould. Gould does not mention hydrogen detection.

U.S. Pat. No. 5,783,153 to Logothetis et al. discloses a sensor made from a metal or its oxide which is capable of changing from one metal or metal oxide phase to another. The oxygen sensitive material disclosed is palladium which changes phase to palladium oxide when the partial pressure of oxygen reaches a certain value. This phase change causes a change in the material's conductivity which can be measured.

U.S. Pat. No. 6,818,525 to Miki et al. teaches the method for producing a semiconductor storage device comprising a hydrogen diffusion preventing layer. The semiconductor storage device comprises a capacitor electrode with a film to reduce the amount of hydrogen reaching the capacitor electrode. Miki discloses the use of palladium oxide as a hydrogen diffusion preventing layer. See FIG. 3 wherein Miki et al. discloses a diffusion layer 302. Miki et al. uses capacitors comprising stacked layers and palladium-oxide as a conductor and not as a dielectric.

U.S. Pat. No. 6,730,270 to O’Connor discloses a single-chip hydrogen sensor wherein a silicon-based hydrogen sensor portion is comprised of a first material and an interconnect metallization layer of the same material. The first material taught in the application is a palladium nickel alloy. The interconnect metallization is covered with an oxide or a nitride to make the interconnect metallization inert. See col. 2 ins. 21-36.

U.S. Pat. No. 6,109,094 to Baranzahi et al. teaches the use of a gas sensing device having a semiconductor substrate wherein the semiconductor substrate is covered by an insulator layer on which an intermediate layer is formed, and is subsequently covered by a gas sensing catalytic layer. The semiconductor substrate disclosed in this patent is silicon carbide or diamond. The intermediate layer is a silicide. The device can be operated at 600° C. continuously. Baranzahi et al. indicates at col. 4 ins. 27 et seq. that the voltage-capacitance curve shifts for a MOSI device.

FIG. 1 illustrates a Pd/SiO₂ hydrogen sensor 100 illustrated in an article entitled "Hydrogen Sensing Mechanisms Of Metal-Insulator Interfaces," Acc. Chem. Res. 1998, 31, pp. 249-256, by LARS-GUNNAR EKEDAH, MATS ERIKSSON, and INGEMAR LUNDSTROM. FIG. 1 illustrates a catalytic metal Pd which dissociates molecular hydrogen into atomic or elemental H⁺ which then forms a dipole layer at the interface of the Pd 103 and the SiO₂ 104. SiO₂ is an insulator and a Si substrate 105 is used and is interconnected to ground 102. A voltage 101 is supplied across the device which functions as a capacitor.

FIG. 1B illustrates a Pd layer 104A formed at the interface of the Pd and the insulator SiO₂. Hydrogen (H₂) 109 is dissociated into atomic hydrogen (H⁺) and the magnitude of the dipole layer is dependent on the amount of hydrogen available.


U.S. Pat. No. 5,265,222 to DiMeo, Jr. et al. teaches the use of a hydrogen sensor including a hydrogen-interactive metal film that reversibly interacts with hydrogen to exhibit a detectable change. A thin film hydrogen permeable barrier layer is used to protect the hydrogen interactive layer from deleterious interaction with non-hydrogen species. DiMeo discloses the use of palladium as the thin film permeable barrier and rare earth metals as the hydrogen interactive layer.

In an article authored by Frank DiMeo Jr., Ph.D., entitled "Integrated Micro-Machined Hydrogen Gas Sensor" prepared for and sponsored by the United States Department of Energy, DOE/GO/10451-F, a recountal of existing hydrogen sensing technology is found. The article discloses (at page 5
thereof) a gated field effect transistor like structure having a floating gate that is coated with a catalyst, typically palladium. As the palladium gate absorbs hydrogen the potential of the gate changes and modulates the conductance of the channel. Dr. Dimeo goes on to indicate that the device is quite sensitive but tends to saturate at low levels of hydrogen making it unsuitable for explosive limit detection. The article goes on to discuss another hydrogen sensor which is based on resistivity changes that occur as a function of hydrogen content in palladium or palladium alloys. Dr. Dimeo does not indicate the structure of these devices and claims that they were not sensitive.

The article entitled “Development of SiC-based Gas Sensors for Aerospace Applications”, Mat. Res. Soc. Symp. Proc. Vo1. 815, 2004 by G. W. Hunter et al. discloses the use of chrome carbide as a barrier layer between the catalytic metal and the SiC semiconductor. Although this composition showed no indication of massive silicide formation between the catalytic sensing layer and the semiconductor substrate, this sensor showed limited sensitivity to hydrogen and showed signs of chromium migration to the surface as well as formation of chromium oxide. Use of catalytically active resistors is based on the concept that hydrogen migrates into the resistor and changes the resistance of the sensor. Palladium and its alloys are common resistor materials. The use of palladium as the hydrogen sensitive metal is problematic because a phase change occurs at high hydrogen concentrations. Use of palladium, however, at low hydrogen concentrations does not cause a phase change to occur and Pd alloys can be used for higher hydrogen concentration measurements. See the article entitled “The Development of Hydrogen Sensor Technology at NASA Lewis Research Center, NASA-Technical Memorandum-106141 (1992) by G. W. Hunter et al.

There is a growing demand for high temperature gas sensors with high sensitivity for engine emission monitoring, fire detection, and fuel leak detection. In particular, high temperature gas sensors having high sensitivity are of interest for aerospace applications including: monitoring emissions from high temperature combustion systems or chemical processing applications, monitoring of fuel leaks in launch vehicles, and fire detection on-board commercial and space vehicles.

A Schottky diode sensing structure can be used to measure hydrogen concentrations even below the limit of detection due to its high gas sensitivity. A Schottky diode can be generally defined as a metal in contact with a semiconductor (MS) or a metal in contact with a thin insulator (MIS) or oxide (MOS) on a semiconductor.

Hydrogen (H₂) dissociates on the surface of the metal leading to the formation of a dipole layer at the interface of the metal and the semiconductor lower layer. The dipole layer leads to a change in the forward or reverse current and a change in the capacitance. The height of the potential barrier is a function of the materials used and their temperature. See the article entitled “Development of SiC Gas Sensor Systems,” NASA/TM-2002-211707 by Hunter et al. The barrier height depends on the work function of the metal and the electron affinity of the semiconductor. Further, use of a Schottky diode allows hydrogen to be detected without requiring high voltage. A small change in the concentration of hydrogen can be reliably detected.

The article entitled “Development of SiC Gas Sensor Systems”, NASA/TM-2002-211707, by G. W. Hunter et al. discloses two structures to improve the stability of the palladium based Schottky diode structures over that of the Pt/SiC Schottky Sensor. The first structure includes the incorporation of chemically reactive oxides such as SnO₂ (tin oxide) for a MOS device. SiC devices can be operated at high temperature to be reactive to hydrocarbons resulting in a MOS (metal reactant oxide semiconductor) Ti oxide (SnO₂) is cited in the article as a reactive oxide. The second structure is PtCr/SiC which has shown good response and stability for some samples but for others has the drawback of silicide formation at the interface of the metal and the semiconductor. The article also mentions a wide variety of materials sensitive to hydrocarbons that may be used without specifying them.

The temperature range for hydrogen detection as identified hereinabove is beyond the upper limit for substrates made from Silicon-based semiconductor substrates. The use of silicide allows for hydrogen detection in the demanding range of conditions required in aerospace applications. Although silicon carbide has excellent high temperature performance, the sensitivity of the device is limited by the reliability and stability of the interfaces between the silicon carbide semiconductor substrate layer and the other layers of the device. At high temperatures, reactions between the various different layers can lead to the formation of silicide materials. These reactions lead to reduced sensitivity and disruptions of the device. The reaction between the layers is a problem for high temperature application requirements where it is difficult to optimize both sensitivity and stability of the device.

In addition to diodes, other devices including capacitors, Metal-Oxide-Semiconductor-Field-Effect-Transistors (MOSFETS), Metal Semiconductor Field Effect Transistor (MESFET), and Metal-Insulator-Semiconductor-Effect Field Effect Transistor (MISFET) are used as gas sensors. Catalytic metals are used as gates for gas sensitive field effect devices. In addition to the gate, these devices typically contain electrodes, a source and a drain, interconnected by a channel region. The channel carries current between the source and the drain. Varying potential of the gate can cause the current flowing in a MESFET structure. In MISFET devices, a gate insulator material is located between the gate electrode and the channel.

Generally, a metal oxide is located between the gate electrode and the channel in a MOSFET structure. Use of a catalytic sensing metal, for example palladium, in the gate allows hydrogen detection to occur when the hydrogen gas is disassociated into atomic hydrogen and adsorbed onto and into the catalytic sensing metal causing a change in the electronic properties of the device.


At high temperatures many gas detecting sensors are not able to maintain sensitivity and stability due to chemical reactions occurring between the catalytic metal sensing layer and substrate layer or between the catalytic sensing layer, barrier layer, and substrate layer. Typically, reactions between the layers of the gas detecting device can lead to the formation of metal silicides on the interface between the metal or metal alloy layer and the substrate layer. The silicide materials which may form render the overall sensor insensitive to hydrogen and hydrocarbon materials. As a result, formation of silicide materials leads to decreasing hydrogen and hydrocarbon detection sensitivity, undesired oxidation, disruption, and degradation of the sensor device. Silicides are understood to incapacitate the sensor. At the same time, to be an effective
When a palladium/palladium oxide/silicon carbide capacitor is arranged as a MOSFET (metal oxide semiconductor field effect transistor) the palladium oxide layer is greater than 200 Angstroms thick and is non-conductive. As the hydrogen concentration of the hydrogen-laden palladium layer increases, the capacitance for a given applied voltage changes (or put another way shifts) which modulates the current flow between the source and the drain in a channel in the n-type epitaxy of the silicon carbide substrate. A voltage is applied across the source and drain. The source and drain are sometimes referred to herein as the first and second electrodes.

The substrate layer consists of a n-type semiconductor such as n-type silicon carbide. The excellent high temperature properties of silicon carbide enabled it to serve as a durable substrate in the device for high temperature applications in the range of at least 450-600 °C.

The barrier interlayer consists of a stable material to prevent unwanted reaction products between the catalytic sensing layer and the substrate layer at high temperatures. The barrier interlayer consists of palladium oxide, a highly stable metal oxide. The palladium oxide is applied by back side deposition techniques. PdO₂ can form naturally from Pd in Pd based gas sensors and can disrupt the gas sensor when formed in-situ in a highly uncontrolled manner. However, when palladium oxide is applied in a controlled manner by standard deposition techniques, an effective layer is created which prevents the formation of silicides.

The use of PdO₂ was demonstrated by observing the oxidation and degradation of PdO₂ on SiC gas sensing structures. After being heated in air at high temperature, metal silicides, PdO₂ and Cr₂O₃ can form from the Pd/Cr/SiC sensor. The Cr₂O₃ migrated toward the sensor surface but it was observed that any PdO₂ that formed and remained at the interface appeared to prevent further formation of metal silicides. The PdO₂ layer that was formed by PdCr reacting in an oxidizing environment in an uncontrolled process did not prevent disruption of the sensor structure leading to sensor degradation. However, it was found that placing PdO₂ in the structure in a controlled and uniform manner provides a stable barrier layer that does not degrade in oxidizing environments and prevents formation of metal silicides. The fabrication of one Schottky diode sensor which did not degrade in oxidizing environments and prevents formation of metal silicides was tested. In words, this implies that two or more types such as 4H or 3C.

The SiC substrate (400 microns thick) is deposited with backside contact Ti and Ni first, the substrate can then be patterned with photolithography and a Schottky diode mask is formed to form the desired diode pattern examples disclosed herein. After deposition of PdO₂ and the gate metals/metal alloys, a lift-off process completes the Schottky diode fabrication. The result, based on testing, was a high sensitivity Pt/PdO₂/SiC sensor with prolonged stability and represents a marked improvement over a Pt/SiC Schottky diode sensor which did not have the PdO₂ layer. Surface analysis was conducted on the tested PdO₂ based sensor and no significant silicide formation was observed. In other words, this implies that two of the major reasons for sensor degradation, silicide formation and migration, are significantly inhibited.

The barrier layer of PdO₂ prevents and minimizes chemical reaction between the catalytic sensing layer (metal or metal alloy) and the substrate layer (SiC). This approach reduces reaction products whose formation previously contributed to the disruption of the sensor structure and by controlling its...
formation and position in the gas sensor structure uses it to improve sensor stability and sensitivity. The PdO layer is very stable and is potentially reduced to Pd through combination with atomic hydrogen. It is believed, but has not yet been verified, that this would likely increase the sensitivity of the device by creating more Pd. Oxidation of the barrier layer which is sometimes problematic with other barrier layers is not an issue with PdO, because it is already oxidized.

Palladium oxide prevents formation of metal silicides, an unwanted reaction product which forms between the catalytic sensing layer and the substrate layer. These silicide materials can adversely affect the sensitivity of the hydrogen detection.

Gas sensors with high sensitivity necessary for engine emission monitoring, fire detection, and fuel leak detection must be stable for operation at temperatures from 450 to 600°C. With the use of palladium oxide as a barrier layer between the catalytic sensing layer (metal layer) and the substrate layer (semiconductor), formation of metal silicides can be prevented while maintaining high sensitivity and prolonged stability of the device.

A method for making the gas sensor is also disclosed and claimed. The steps for making a gas sensing diode include: preparing an n-type substrate such as a semiconductor wafer chip mass-fabrication can be used by way of example in a capacitor structure. Alternatively, the palladium oxide may be produced by wet chemistry.

A method for using the hydrogen or hydrocarbon gas sensor present at high temperatures is also disclosed and claimed. The method comprises the steps of: (1) applying a bias voltage across the top contact and bottom contact layers of a Schottky diode where the diode is comprised of a top metal or metal alloy layer, an n-type substrate layer, and a barrier layer comprising a palladium oxide located between the metal or metal alloy layer and substrate layer, and, measuring the current in gaseous hydrogen or hydrocarbons. Methods for using the invention in the form of a capacitor (MOS) and in the form of a transistor (MOSFET) are also disclosed herein.

The gas sensing structure has been developed for detection of hydrogen or hydrocarbon gas at temperatures in the range of at least 450-600°C. The stable composition of gas sensing structure prevents unwanted reaction between the catalytic sensing layer and the substrate layer at higher temperatures. Disruption of the operation of the device at high temperature due to the formation of metal silicides and oxidative degradation of the sensor is also prevented.

The layers of the device are assembled in a miniaturized Schottky diode hydrogen and hydrocarbon sensor. The sensor has high sensitivity based on the stability of the barrier interlayer which prevents unwanted reactions between the catalytic sensing layer and the substrate layer. Detection of extremely low levels of hydrogen gas and hydrocarbon gas is possible due to the high sensitivity of the device. Optimal voltage levels can be used without requiring high voltage to detect hydrogen or hydrocarbon gas. The sensor of the present invention is a high gain device.

The miniaturized Schottky diode hydrogen and hydrocarbon sensor with the structure of catalytic sensing layer—barrier interlayer—substrate (metal-metal oxide—silicon carbide) is fabricated with semiconductor microfabrication techniques. The inclusion of the palladium oxide barrier interlayer between the catalytic metal layer and the substrate layer allows for a device that has long term stability at high temperatures while maintaining high sensitivity and fast response time. The device is small in size and easy to fabricate. Semiconductor wafer mass-fabrication can be used to produce the device cost effectively. Further, the unique structure of the device including its high sensitivity, stability, and small-size allows for effective and versatile use in numerous applications.

It is an object of the present invention to provide a miniaturized Schottky diode hydrogen and hydrocarbon sensor with the structure of catalytic metal layer—palladium oxide barrier interlayer—silicon carbide (SiC) substrate layer.

It is a further object of the present invention to provide a miniaturized Schottky diode hydrogen and hydrocarbon sensor having a stable and sensitive palladium oxide barrier layer.

It is a further object of the present invention to provide a miniaturized Schottky diode hydrogen and hydrocarbon sensor capable of operating in the temperature range of at least 450-600°C.

It is a further object of the present invention to provide a sensor structure that is able to be used in a variety of electronic measurement applications where high stability, high sensitivity, and small size are required.

It is a further object of the present invention to provide a material which is stable at high temperatures and prevents reactions between a catalytic sensing layer and the substrate layer of a sensor at high temperatures.

It is a further object of the present invention to provide a material for use in a sensor which is sensitive to hydrogen gas and gaseous hydrocarbons and resistant to oxidative degradation at high temperatures.

It is an object of the present invention to provide a hydrogen sensor which does not form silicides that migrate throughout the device.

It is an object of the present invention to provide a Schottky diode comprising a catalytic metal on top of a palladium oxide interlayer which is sandwiched between the catalytic metal and the semiconductor.

A better understanding of these and other objects of the invention will be had when reference is made to the Brief Description Of The Drawings and the Claims which follow hereinafter.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a schematic presentation of a prior art Pd/SiO$_2$/Si hydrogen sensor.

FIG. 1A is a capacitance versus voltage plot of the sensor of FIG. 1.

FIG. 1B is a schematic representation of the dipole formed at the interface of the Pd and the SiO$_2$.

FIG. 2 is a current and voltage sweep of the Pt/PdO$_2$/Si hydrogen diode sensor of the instant invention.

FIG. 2A is a current and voltage sweep of the Pd/PdO$_2$/SiC hydrogen diode sensor of the instant invention.

FIG. 3 is a cross-sectional view of the invention illustrating the catalytic metal layer, the palladium oxide barrier interlayer, and the substrate layer with an applied direct current voltage.

FIG. 4 is a cross-sectional view of the invention illustrating the metal layer, the palladium oxide interlayer, and the substrate layer used by way of example in a capacitor embodiment.
FIG. 5 is a cross-sectional view of the invention illustrating the catalytic metal layer, the palladium oxide barrier layer, and the substrate layer used by way of example in a diode embodiment.

FIG. 6 is a cross-sectional view of the invention used by way of example illustrating the metal(s) or metal alloy gate layer, the palladium oxide layer, and the substrate layer in a transistor embodiment.

FIG. 7 is a graph of current output for air, 0.5% hydrogen in nitrogen and gain vs. time of the Schottky Diode Pt/PdO/SiC Tested at 450°C with a forward bias of 0.4 VDC.

FIG. 8 is a graph of current output for air, 0.5% hydrogen in nitrogen and gain vs. time of the Schottky Diode Pt/PdO/SiC Tested at 450°C and 600°C with a forward bias of 1.0 VDC.

A better understanding of the drawings and invention will be had when reference is made to the Description of the Invention and Claims which follow hereinafter.

DESCRIPTION OF THE INVENTION

The present invention comprises a miniaturized Schottky diode hydrogen and hydrocarbon sensor with the structure of catalytic sensing metal-palladium oxide barrier interlayer-semiconductor substrate layer to detect hydrogen and hydrocarbon gases at elevated temperatures. The metal-metal oxide-semiconductor structure provides a stable and sensitive hydrogen gas detection device that is resistant to oxidative degradation and silicide formation. The sensitivity of the device is achieved through the use of a metal such as platinum or palladium in the catalytic sensing layer which is sensitive to hydrogen and hydrocarbons but resistant to significant oxidation. The barrier interlayer is resistant to oxygen and prevents reaction between the catalytic sensing metal layer and the semiconductor substrate layer. These unwanted reactions lead to the formation of silicides which affect the surface states of the SiC interface. As a result, formation of silicide can lead to disruption of the layers and reduce the overall performance of the device including reduced sensitivity and stability. The palladium oxide barrier interlayer allows stable operation of the device at high temperatures as a voltage is applied across the top and bottom layers of this device. By stability, it is meant that a significant chemical reaction between the catalytic metal layer and the semiconductor substrate does not occur. By barrier it is meant a chemical barrier not to be confused with the term potential barrier which is relevant to the metal-semiconductor junction of a Schottky diode.

The catalytic sensing layer shows changes in the current voltage curve in the diode application and/or changes in capacitance for a given voltage in the MOS capacitor or MOSFET transistor applications.

FIG. 2A is a current and voltage sweep 200A of a Pt/PdO/SiC hydrogen diode sensor of the instant invention at 450°C. at 467 hours of operation. The current in air is denoted by reference numeral 201, and the current in an atmosphere of 0.5% hydrogen gas with the balance being nitrogen is denoted by reference numeral 202. From FIG. 2A it can be seen that the gain in the reverse bias sense is stable (approximately constant) between voltages of 0 and ~10 VDC. It can also be seen that high gain and high current outputs are achieved when forward bias is applied. Gain is defined here as the current output of the sensor in hydrogen divided by the current output of the sensor in air. The sensitivity of the device is high with sensitivity being defined here as the change of the output in hydrogen as compared with air.

FIG. 2 is a current and voltage sweep 200A of a Pt/PdO/SiC hydrogen diode sensor of the instant invention at 450°C. at 715 hours of operation. The current in air is denoted by reference numeral 201A and the current in an atmosphere of 0.5% hydrogen gas with the balance being nitrogen is denoted by reference numeral 202A. From FIG. 2A it can be seen that the gain in the reverse bias sense is stable (approximately constant) between 0 and ~6 VDC. It can also be seen that high gain and high current outputs are achieved at the threshold voltage in the forward bias sense yielding a similar high gain and sensitivity. Gain is defined here as the current output of the sensor in hydrogen divided by the current output of the sensor in air.
200 Angstroms. The n-type epitaxial layer 403 is located on top of the SiC wafer 404 followed by the backside contact 405. In this capacitor embodiment, the palladium oxide is not electrically conductive, and, therefore, no current flows through the device. The metal 401 is typically palladium or platinum. A voltage is applied across the sensor between the metals 501, 505 and the capacitance of the sensor is modulated by hydrogen or hydrocarbon interaction with the dipole moment formed at the interface of the metal 401 and the palladium oxide.

FIG. 5 is a cross-sectional view of the diode 500 illustrating the metal(s) or metal alloys layer 501, the PdO, layer (50 Angstroms to 200 Angstroms in thickness) 502, n-type epitaxial layer 503 of the silicon carbide, SiC wafer 504, and the backside contact 505 similar to FIG. 3 absent the applied 600 VDC. Reference numeral 702 represents the current in hydrogen or hydrocarbon gain. From 610 to 680 hours at 450°C, 715 hours of operation. The plot of hydrogen 702 versus air 701. 450°C, 715 hours of operation. FIG. 5 illustrates the n-type epitaxial layer 503 of the silicon carbide. As stated previously, the silicon carbide is formed sensors including 405. In this capacitor embodiment, the palladium oxide is not referred to herein as the first and second electrodes.

FIG. 7 illustrates current output in microamps of a Schottky diode consisting of a palladium/palladium oxide/silicon carbide structure tested at 450°C with a forward current at a bias voltage of 0.4 VDC. FIG. 7 is a plot of current output (μA) of the diode of the invention at 450°C with a forward bias of 0.4 VDC. Reference numeral 702 represents the current in the diode for hydrogen at 0.5% concentration and reference numeral 701 represents the current in the diode for air at 450°C with a forward bias of 0.4 VDC. Gain 703 (current in hydrogen/current in air) is also illustrated in FIG. 7. The plot illustrates stable measurement of the current in air and 0.5% hydrogen over a period of approximately 1400 hours of operation. The hydrogen was used along with nitrogen in the plot of FIG. 2. The high sensitivity and gain is illustrated by the plot of hydrogen 702 versus air 701.

FIG. 8 illustrates the current output in microamps of a Schottky diode comprising a platinum/palladium oxide/silicon carbide structure tested at alternating temperatures of 450°C and 600°C with a forward bias voltage of 1.0 VDC. From 0 to 169 hours at 450°C reference numeral 801 is the gain, reference numeral 802 is the current in air and reference numeral 803 is the current in hydrogen. From 170 to 216 hours at 600°C reference numeral 804 is the gain, reference numeral 805 is the current in air, reference numeral 806 is the current in hydrogen. From 217 to 609 hours at 450°C reference numeral 807 is the current in air, reference numeral 808 is the gain, and reference numeral 809 is the current in hydrogen. From 610 to 680 hours at 600°C reference numeral 810 is the current in air, reference numeral 811 is the gain, and reference numeral 812 is the current in hydrogen. Overall, although changes occurred in the baseline when the sensor is first introduced to 600°C (a break-in period), FIG. 8 illustrates high gain, high sensitivity, and stability in the alternating temperature test over time.

The process steps of making the Schottky diode comprises the following steps: preparing a n-type semiconductor substrate layer (approximately 400 microns in thickness) n-type silicon carbide (SiC) by cleaning, depositing backside contacts, applying photoresist and a Schottky diode photomask, controlled reactive sputter deposition (or evaporation) of approximately 50 Angstroms of palladium onto a target in an O₂ (oxygen) atmosphere on the silicon carbide substrate layer, and, sputter deposition of 430 Angstroms of a metal or metal alloy selected from the group consisting of Pt, Pd, Au, Ir, Ag, Ru, Rh, In, Os, Cr, Ti, and alloys of these metals with each other on top of said metal oxide layer. Alternatively, the palladium oxide may be evaporated onto the silicon carbide substrate. Lift-off processes and etching is employed as necessary. The oxygen atmosphere may be withheld for a few seconds to prevent the formation of silicon dioxide on the silicon carbide.

Traditional photolithographic processes may be used to form sensors including the application of photoresist, masks, applying light to imidize portions of the photoresist, wet and dry etching, etc. The catalytic sensing layer and the barrier layer may also be deposited using the sol-gel method, reactive deposition, and chemical vapor deposition in addition to sputtering.

DESCRIPTION OF REFERENCE NUMERALS

100 Prior art capacitor
100 A Capacitance-Voltage curves
100 B Dipole illustration
101 Applied DC Voltage
102 Ground potential
103 Palladium
104 Silicon dioxide insulator
104 A Dipole moment at the interface of palladium and silicon dioxide
105 p-type silicon
106 Capacitance-Voltage curve without hydrogen
107 Capacitance-Voltage with hydrogen
108 Dipole
109 Hydrogen
110 Dipole represented as a differential voltage
200 Current and voltage Sweep of Pd/PdO/SiC at 450°C, 467 hours of operation
201 Current measured in air
202 Current measured in 0.5% hydrogen gas
200 A Current and voltage sweep of Pd/PdO/SiC at 450°C, 715 hours of operation
201 A Current measured in air
202 A Current measured in 0.5% hydrogen gas
300 Gas Detecting Diode with Applied Voltage
301 Metal(s) or Metal Alloys Layer
302 PdO, (barrier layer)
303 SiC Layer
304 Backside Contact
305 Amplifier
306 Voltage polarity reference
307 Voltage polarity reference
308 DC Voltage
309 Hydrocarbons
310 Hydrogen
320 Capacitor
401 Metal(s) or Metal Alloys Layer
402 PdO, Layer
403 n-type epit layer
404 SiC wafer
405 Backside Contact
500 Diode
501 Metal(s) or Metal Alloys Layer
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502 . . . PdO, Layer
503 . . . n-type epi Layer
504 . . . SiC Wafer
505 . . . Backside Contact
600 . . . Transistor
601 . . . Metal(s) or Metal Alloy(s) Layer
602 . . . PdO, Layer
603 . . . n-type epi layer
604 . . . SiC p-type
605 . . . Backside contact
606 . . . Source
607 . . . Drain
700 . . . Graph of Current Output (Hydrogen and Air) and Gain vs. Time for Schottky Diode Pd/PdO, /SiC
701 . . . Current in air
702 . . . Current in Hydrogen
703 . . . Gain
800 . . . Graph of Current Output and Gain vs. Time for Schottky Diode Pd/PdO, /SiC
801 . . . Gain 0 to 169 hours, 450° C.
802 . . . Current in air, 0 to 169 hours, 450° C.
803 . . . Current in 0.5% hydrogen, 0 to 169 hours, 450° C.
804 . . . Gain 170 to 216 hours, 600° C.
805 . . . Current in air, 170 to 216 hours, 600° C.
806 . . . Current in 0.5% hydrogen, 170 to 216 hours, 600° C.
807 . . . Current in air, 217 to 609 hours, 450° C.
808 . . . Gain 217 to 609 hours, 450° C.
809 . . . Current in hydrogen, 217 to 609 hours, 450° C.

810 . . . Current in air, 610 to 680 hours, 600° C.
811 . . . Gain, 610 to 680 hours, 600° C.
812 . . . Current in hydrogen, 610 to 680 hours, 600° C.

Although this invention has been described by way of example and with particularity and specificity, those skilled in the art will recognize that many changes and modifications may be made without departing from the spirit and scope of the invention defined by the Claims which follow hereinbelow.

We claim:

1. A gas sensor comprising: a metal layer approximately 150 to 1000 Angstroms thick selected from the group consisting of Pt, Pd, Au, Ag, Ru, Rh, In, Os, Cr and Ti; a PdO, barrier layer approximately 50 to 200 Angstroms thick; and, a SiC substrate layer; and, said barrier layer residing between said metal layer and said SiC substrate layer.

2. A gas sensor as claimed in claim 1 wherein said SiC substrate layer is approximately 400 microns thick.

3. A gas sensor as claimed in claim 1 wherein said metal layer is alloyed with another metal selected from the group consisting of Pt, Pd, Au, Ir, Ag, Ru, Rh, In, Os, Cr, and Ti.

4. A gas sensor as claimed in claim 1 wherein said metal layer is immersed in an atmosphere containing hydrogen and/or hydrocarbons and a voltage is applied across said metal layer and said substrate producing a current through the gas sensor proportional to the hydrogen and/or hydrocarbon content of the atmosphere.

5. A gas sensor as claimed in claim 1 wherein said metal layer is alloyed with another metal selected from the group consisting of Pt, Pd, Au, Ir, Ag, Ru, Rh, In, Os, Cr, and Ti.